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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the manufacture method of the negative electrode for non-drainage system rechargeable batteries of giving the cycle property excellent in the high capacity using the sintered compact which makes silicon an active material as an electrode material.

[0002]

[Description of the Prior Art] The high capacity lithium secondary battery containing the positive active material which can insertion emit a lithium ion, and a negative-electrode active material attracts attention with the spread of a cellular phone, notebook computers, etc. Although the negative electrode using the nature material of a baked carbon as a negative-electrode active material is put in practical use, the negative-electrode active material which has much more high capacity is called for.

[0003] Then, the attempt which constitutes a negative electrode from nature material of a baked carbon, using the silicon which can expect high capacity as a negative-electrode active material is made. for example, the method of adding and casting the graphite and the binder of electric conduction material to JP,7-29602,A, using Li_xSi ($0 \leq x \leq 5$) as a negative-electrode active material, considering as a pellet, and manufacturing a negative electrode by using an electroconductive glue as a charge collector -- moreover -- JP,5-74463,A -- a silicon single crystal -- as an active material -- using -- a nickel mesh -- **** -- the method of manufacturing a negative electrode by things is indicated

[0004] Moreover, these people have proposed using for a negative electrode the sintered compact which consists of complex of silicon and carbonaceous material in WO 98/No. 24135 official report. The sintered compact which silicon and carbonaceous material compounded is obtained by heating silicon or its compound, and the organic material and/or carbon material that can be carbonized by heat-treatment under a non-oxidizing atmosphere.

[0005]

[Problem(s) to be Solved by the Invention] However, while the negative electrode which used silicon for the active material gives high capacity in early stages of charge and discharge, there is a fall of the capacity accompanying the repeat of charge and discharge, and in order to be highly efficient-ization, improvement in much more cycle property is desired.

[0006] Then, this invention made silicon the negative-electrode active material, and aimed at offering the manufacture method of a non-drainage system rechargeable battery negative electrode of giving the cycle property excellent in high capacity. C12

[0007]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, the manufacture method of the negative electrode for non-drainage system rechargeable batteries of this invention forms the paint film which consists of negative-electrode material containing silicon, and a binder which forms a nongraphitizing carbon by heat-treatment on a charge collector, sinters it under a non-oxidizing atmosphere, and is characterized by a charge collector and really carrying out. C14

[0008] A binder is difficult graphitization nature, and it can be made to sinter in the manufacture method of this invention, maintaining the configuration of a paint film, since it becomes an amorphous carbon with few volume changes. Since an amorphous carbon furthermore forms a conductive network in the sintering inside-of-the-body section, the conductivity of a sintered compact can be raised.

Moreover, since a binder carries out solid phase carbonization after the charge collector and the paint film have stuck, the adhesion of a charge collector and a sintered compact improves and reduction of the contact resistance between a charge collector and a sintered compact is attained.

[0009] Here, "the binder which forms a nongraphitizing carbon by heat-treatment" in this invention is explained in full detail. Generally it sees. According to Otani's and others writing "a carbon fiber" (modern edit company **) "like pitch coke that which carbonizes via the shape of liquid serves as a graphitizing carbon, and that which carbonized without a three-dimensions-high polymer like a phenol formaldehyde resin or wood fusing serves as a nongraphitizing carbon" the layer structure made in the carbonization in a thing and a temperature field about 500 degrees C or less It is fundamentally taken over by heat treatment in an elevated temperature, and becoming the difference clearly carried out on the X diffraction parameter for the first time, and appearing by about 2000-degree C high temperature processing, (this work drawing 1 . 21) is known. That is, if it is not what carried out about 2000-degree C high temperature processing, although it is difficult to discriminate whether it is a nongraphitizing carbon or it is a graphitizing carbon, it is fundamentally decided by the true character of each raw material whether become a nongraphitizing carbon.

[0010] Of course, although it can control somewhat intentionally by changing carbonization conditions, it heats, blowing chlorine gas, in order to obtain a nongraphitizing carbon by using a pitch as a raw material, for example, or it is known that sulfur must be twisted to the special method of adding about 5% or more. On the contrary, in order to make it a graphitizing carbon using the material which carbonizes via solid phase originally, being restricted when the stacking tendency of a molecule is changed notably is known by operation of extension etc.

[0011] Concretely, as "a binder which forms a nongraphitizing carbon by heat-treatment" used in this invention, derived protein, such as vinylidene resin, such as saccharides, such as thermosetting resin, such as phenol resin, a furan resin, a urethane resin, an epoxy resin, polyimide resin, melamine resin, and a urea-resin, sugar, starch, and a cellulosic, a polyvinylidene chloride, and a polyvinylidene fluoride, and gelatin, natural protein, other polyacrylonitriles, etc. are mentioned, for example. Also in this, phenol resin, a furan resin, vinylidene resin, a saccharide, a polyacrylonitrile, and gelatin are desirable especially.

[0012] Moreover, in the manufacture method of this invention, the survival rate after sintering of the above-mentioned binder is 10 % of the weight or more more preferably 5% of the weight or more. If a survival rate is 5 % of the weight or more, sufficient adhesion for the contact resistance reduction between a sintered compact and a charge collector is securable. Here, a survival rate is expressed with the ratio of the weight after the heat-treatment to the weight before heat-treatment.

[0013]

[Embodiments of the Invention] Hereafter, this invention is explained in detail. As silicon used for this invention, a crystalline substance and amorphous all can be used and you may use in the form of the compound containing silicon. as a silicon compound -- organic silicon compounds, such as inorganic silicon compounds, such as silicon oxide, and silicone resin, a ** silicon high molecular compound, -- the material which is decomposed or returned by the non-oxidizing atmosphere [like], and may change to silicon is mentioned Also in these, especially silicon powder (simple substance) is desirable. Although especially the purity of silicon powder is not limited, it is desirable that it is 90 % of the weight or more of silicon content in order to obtain sufficient capacity, and 99.999 or less % of the weight of its thing is desirable from economical efficiency. Although especially the particle diameter of silicon powder is not limited, a 0.01-micrometer or more mean particle diameter [100 micrometer or less] thing is suitably used from a homogeneous viewpoint of handling, a raw material price, and negative-electrode material.

[0014] Moreover, it is desirable to also use the material carbonized with a carbon material or heat

treatment in addition to silicon for the negative-electrode material used for this invention. As a carbon material used here, the carbide and such mixture of corks, a glassy carbon, a graphite, and a pitch are mentioned.

[0015] Moreover, what becomes a graphitizing carbon can be used as a material carbonized with heat treatment. A pitch is desirable although the pitch which makes a principal component mixture of condensed-system polycyclic hydrocarbon compounds, such as naphthalene and an acenaphthylene, the derivative of those, or the above-mentioned compound, the resin which serves as a graphitizing carbon with heat treatment further are specifically mentioned. In addition, the material which serves as difficulty graphitized carbon with heat treatment serves as a binder said by this invention, when contained in a paint film.

[0016] You may add polymer and a plasticizer in order to raise the adhesion of a paint film and a charge collector to the binder which forms a nongraphitizing carbon by heat-treatment of this invention. If it considers as the polymer added for this purpose, polyethyleneimine etc. can be used for sugar and a polyvinyl butyral, polyester, acrylic resin, etc. can be used for gelatin for a polyethylene glycol etc. at phenol resin, a furan resin, and a polyacrylonitrile. Moreover, a glycerol etc. can be used, when a polyvinyl butyral is added and gelatin is used for a phthalic ester, an adipate, etc. as a binder as a plasticizer, for example.

[0017] Moreover, you may mix and use the gelatin and sugar which are the binder of this invention. Gelatin can be plasticized even if it does not add a plasticizer by mixing with sugar.

[0018] In the manufacture method of this invention, although it is not limited especially when forming a paint film on a charge collector, the method of applying the coating liquid which carried out wet blending of negative-electrode material and the binder from a viewpoint of homogeneous reservation of a paint film is desirable. Moreover, it exfoliates and the paint film which could apply coating liquid directly on the charge collector, and could form the paint film, or was applied and formed on other bases may be stuck on a charge collector. When sticking the paint film which exfoliated on a charge collector, it is desirable to apply and paint-film-ize coating liquid to the base which is easy to exfoliate. A base can be chosen by conformity with a solvent, a binder, a negative-electrode active material, etc. which are contained in coating liquid. The film made from PET which carried out remover processing is used suitable for the base of this purpose. Lamination of the exfoliative paint film and the exfoliative charge collector may be performed only by sticking by pressure, and may be pasted up using adhesives etc.

[0019] Moreover, it is desirable to mix the liquid which dissolves or distributed the binder uniformly beforehand, and negative-electrode material in order to mix negative-electrode material and a binder uniformly. Arbitrary solvents and arbitrary water can be used for manufacture of the solution of a binder, or dispersion liquid according to the rate of drying of a binder, the polymer added independently and the solubility and dispersibility of a plasticizer, the dispersibility and the solubility of negative-electrode material, and a paint film etc. Moreover, you may add a dispersant in order to raise the dispersibility of the negative-electrode material in coating liquid.

[0020] Moreover, in order to carry out wet blending of negative-electrode material and the binder and to obtain coating liquid, the various dispersers which are the stock-in-trades of coating liquid manufacture, i.e., a roll mill, a ball mill, attritor, a sand mill, the De Dis parser, a jet mill, an ultrasonic disperser, etc. can be used.

[0021] Moreover, in order to apply coating liquid on a charge collector or other bases, various coaters, such as a gravure coating machine, a die coating machine, a dip coater, a blade coating machine, a spin coater, and a spray coater, can be used.

[0022] Moreover, although a hot air drying equipment is desirable in respect of drying efficiency in order to dry the applied coating liquid and to form a paint film, in addition to this, various kinds of dryness methods can be used, without being limited to this.

[0023] Moreover, in order to raise the homogeneity of a paint film, and density, it is desirable to compress the paint film formed on the charge collector if needed with press machines, such as for example, a roll-press machine and a monotonous press machine.

[0024] Moreover, although the gap or one metal chosen from stainless steel, ****, and a platinum group

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can be used for the conductive metal used for a charge collector, it is easy to be returned, conductivity is high, and still cheaper copper is desirable. And although any of a foil or a mesh may be used for a conductive metal, 3-100 micrometers of thickness are desirable.

[0025] Moreover, below the melting point of the conductive metal to be used of the temperature which sinters a paint film is desirable, for example, when using copper, it is 500-1000 degrees C preferably 1083 degrees C or less of melting points. Here, sintering is performed under non-oxidizing atmospheres, such as the argon atmosphere lower, under nitrogen-gas-atmosphere mind.

[0026] Any well-known material can be conventionally used for the positive-electrode material used as a positive active material of this invention, for example, LiCoO_2 , LiNiO_2 , MnO_2 , LiMnO_2 , LiMn_2O_4 , LiMn_2O_4 , $\alpha\text{-V}_2\text{O}_5$, and TiS_2 grade are mentioned.

[0027] The solid polymer electrolyte which made the nonaqueous electrolyte which dissolved the lithium compound of LiPF_6 grade in organic solvents, such as ethylene carbonate and dimethyl carbonate, or the organic solvent which dissolved dissolution or the lithium compound for the lithium compound in the macromolecule hold can be used for the nonaqueous electrolyte used for this invention.

[0028]

[Example] Example 1

The production <manufacture of raw material powder> silicon powder (1 micrometer [of mean particle diameters], 99% [of purity], made in High grade Chemical research Center) 80 weight section of a negative electrode The 20 sections were mixed in the mixed-powder end (the graphite 90 section / pitch resin 10 section, made in Osaka Chemicals) of (the weight section is hereafter abbreviated to the section), graphite, and a pitch resin, the vibration mill ground for 5 minutes after 3-hour baking at 1100 degrees C under nitrogen-gas-atmosphere mind, and raw material powder was obtained.

[0029] <Analysis of a binder> When thermogravimetric analysis of the polyvinylidene fluoride (product made from Kureha Chemistry) of a binder was carried out under nitrogen-gas-atmosphere mind, the weight survival rate in 800 degrees C was 25%.

[0030] <Manufacture of coating liquid> The N-methyl-2-pyrrolidone solution (10%) 70 section of a polyvinylidene fluoride was added to the raw material powder 30 section, and it mixed for 10 minutes by the vibration mill, and considered as coating liquid.

[0031] <production of a paint film> -- an applicator (gap 500micrometer) -- using -- coating liquid -- a copper foil (30 micrometers in thickness) top -- applying -- 80 degrees C -- after the dryness during 30 minutes, and the diameter of 2cm -- it judged circularly, and was stuck by pressure with the monotonous press machine, having put the pressure of 1.5 t/cm², and the paint film was obtained

[0032] <Baking of a paint film> The paint film was calcinated at 800 degrees C under nitrogen-gas-atmosphere mind for 3 hours, and was used as the negative electrode.

[0033] 1t /of mixture which consists of the evaluation cobalt acid lithium 88 section of a negative electrode, the acetylene black 6 section, and the polytetrafluoroethylene resin 6 section was cast by the pressure of 2 cm, and the positive electrode of the shape of a disk with a diameter of 2cm was obtained.

[0034] To the thing (Mitsubishi Chemical make) and separator which dissolved LiPF_6 in the electrolytic solution to the concentration of 1 mol/l at the mixed solvent of the volume ratio 1:1 of ethylene carbonate and dimethyl carbonate, the coin cell was produced using the porous polyethylene film (Asahi Chemical Industry Co., Ltd. make) with a thickness of 25 micrometers, the above-mentioned positive electrode, and the negative electrode. And the 2mA constant current performed the charge and discharge test after aging at the room temperature for 36 hours. A result is shown in Table 1.

[0035] Thermogravimetric analysis of the example 2. polyacrylonitrile (molecular weight 150,000, Polyscience reagent) was carried out by the same method as an example 1. The weight survival rate in 800 degrees C was 35%.

[0036] Except having diluted the polyacrylonitrile 6 section and the polyvinyl-butyril (Sekisui Chemical Co., Ltd. make) 2 section with the N-methyl-2-pyrrolidone 60 section, and having added to the raw material powder 32 section, using this polyacrylonitrile as a binder, the negative electrode was produced by the same method as an example 1, and the coin cell was produced. The result of a charge and

discharge test is shown in Table 1.

[0037] Thermogravimetric analysis of the example 3. phenol-formaldehyde resin (resol type and viscosity 50 Pa-s) was carried out by the same method as an example 1. The weight survival rate in 800 degrees C was 60%.

[0038] Except having dissolved the polyvinyl-butylal 5 section used in the phenol-formaldehyde resin 7.5 section and the example 2 in the ethanol 50 section, using this phenol-formaldehyde resin as a binder, and having added to the raw material powder 37.5 section, the negative electrode was produced by the same method as an example 1, and the coin cell was produced. The result of a charge and discharge test is shown in Table 1.

[0039] Thermogravimetric analysis of the gelatin (product made from Nitta Gelatin) was carried out by the same method as an example 1. The weight survival rate in 800 degrees C was 20%.

[0040] Except having dissolved the gelatin 12.5 section and the glycerol (Wako Pure Chem reagent) 2.5 section in the water 50 section, and having added to the raw material powder 35 section, using this gelatin as a binder, the negative electrode was produced by the same method as an example 1, and the coin cell was produced. The result of a charge and discharge test is shown in Table 1.

[0041] Thermogravimetric analysis of the example 5. granulated sugar (Taito Co., Ltd. make) was carried out by the same method as an example 1. The weight survival rate in 800 degrees C was 17%.

[0042] Except having dissolved the granulated sugar 11 section in the water 44 section, and having added to the raw material powder 35 section with the polyethyleneimine solution (NIPPON SHOKUBAI Co., Ltd. make) 10 section 30%, using this granulated sugar as a binder, the negative electrode was produced by the same method as an example 1, and the coin cell was produced. The result of a charge and discharge test is shown in Table 1.

[0043] When the material used as a nongraphitizing carbon was used for a binder, as shown in examples 1-5, the capacity of a cell was high and the fall of the capacity accompanying charge and discharge was very small.

[0044]

[Table 1]

	初期放電容量 (mAh)	30サイクル目の放電 容量 (mAh)
実施例1	25	24
実施例2	26	25
実施例3	26	25
実施例4	26	25
実施例5	26	25

[0045]

[Effect of the Invention] The manufacture method of the negative electrode for non-drainage system rechargeable batteries of giving the cycle property excellent in high capacity can be offered by forming the paint film which consists of negative-electrode material containing silicon, and a binder which forms a nongraphitizing carbon by heat-treatment on a charge collector, sintering under a non-oxidizing atmosphere, and uniting with a charge collector so that clearly from the above explanation.

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture method of the negative electrode for non-drainage system rechargeable batteries which forms the paint film which consists of negative-electrode material containing silicon, and a binder which forms a nongraphitizing carbon by heat-treatment on a charge collector, sinters under a non-oxidizing atmosphere, and is united with a charge collector.

[Claim 2] The manufacture method of the negative electrode for non-drainage system rechargeable batteries according to claim 1 which is at least one sort chosen from the group which the above-mentioned binder becomes from phenol resin, a furan resin, vinylidene resin, a saccharide, a polyacrylonitrile, and gelatin.

[Claim 3] The manufacture method of the negative electrode for non-drainage system rechargeable batteries according to claim 1 or 2 that the survival rate after sintering of the above-mentioned binder is 5 % of the weight or more.

[Translation done.]